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T. Yamamoto

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PCDDs and PCDFs in Paper Products

Takeshi YAMAMOTO

(Osaka City Institute of Public Health and Environmental Sciences)

With regard to the environmental problems of chlorinated dioxins (Note 1), many sources have been identified such as impurities in chemical products (PCB, chlorinated herbicides, chlorophenol preservatives, etc.), improper treatment of chemical wastes, fire in PCB transformers, or the byproducts from the burning and incineration of various waste products, etc.; then in December 1983 the United States Environmental Protection Agency (US EPA) set up a "Dioxin Strategy" in order to identify the proliferation and sources of chlorinated dioxins, and investigations were begun.[1)]

As the target of the investigations, the actual pollution levels of 2,3,7,8-tetrachloro-dibenzodioxin (2,3,7,8-TCDD), the most toxic of the compounds where its effects are of concern, were investigated in seven levels (Tiers) according to the possible pollution sources. In Tiers 1 and 2 the investigations were carried out at the production sites of 2,4,5-trichlorophenol (2,4,5-TCP), at pesticide production sites which use 2,4,5-TCP as a starting material and at their waste treatment sites, with the intended objective of removing 2,3,7,8-TCDD pollution.

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Tier 3 encompasses the investigations at sites where 2,4,5-TCP and its derivatives are used as pesticides, and at waste treatment sites of related wastes, while Tier 6 are the investigations of facilities where chemical compounds and pesticides, etc. were polluted with the 2,3,7,8-TCDD produced because of improper production processes; in less than 10% of the facilities the soil was polluted with greater than 1 ppt of 2,3,7,8-TCDD.

Tier 4 includes the pollution sources from incinerations, which are the sewage soil incineration facilities, black liquor boilers of paper mills, lumber incineration (including waste lumber) facilities, metal-recycling factory incineration facilities, and other incineration facilities, etc. The city waste waste incinerators have been specially identified as a source, and therefore are not investigated here.

Tier 5 is where the pesticide 2,4,5-TCP was used or is being used commercially, and at these locations it was detected in 15 out of 26 cases, with their levels being 0.6-6623 ppt in the soil, 0.7-200 ppt in bottom matter, and 8-47 ppt in fish.

Tier 7 included the control areas which were considered not to be polluted by 2,3,7,8-TCDD, but it was found in 17/221 in city soil, and in 1/138 in countryside soil, with 11.2 ppt detected; and the detection ratio in fish (particularly in the five Great Lakes) was high, where the highest concentrations were in whole fish (85 ppt) and in the edible sections (41 ppt). Also, as an unexpected source, in the effluent water from paper and paper mills, 2,3,7,8-TCDD was detected, and the paper production industry was identified as the source.

Thus, the recognition that chlorinated dioxins are produced during paper and pulp production was reported for the first time in this study by the US EPA. At Dioxin '86 (Fukuoka) where a summary of this was published,

Rappe *et al.* reported that in Sweden on the coast close to the pulp industry, the pollution by chlorinated dioxins occurs with specific isomer patterns in the bottom matter and in crabs.[2] In the following year at Dioxin '87 (Las Vegas), in addition to the United States and Sweden, cases that occurred in Canada were reported. These reports acted as a trigger to spur on the carrying out of many other investigations and research, and so at Dioxin '88 which was held in August 1988 at Umeo, Sweden, there were 16 reports presented which were related to this area; besides its release to the environment from the paper and pulp milling industry, attention has been drawn to the spread of chlorinated dioxins to far-reaching areas such as the possibility of transfer to foods from daily used paper products and paper containers, etc. Presented here are the topics dealing with paper products and chlorinated dioxins, based on the findings of Dioxin '88, which we attended with the support of research funds from this Association.

Production of Chlorinated Dioxins during the Pulp Treatment Process

The isomer composition of chlorinated dioxins found in the environment is also generally referred to as the "incineration pattern", and this is quite different from the isomer compositions found in pulp effluents and paper products (see Figure 1). p.44

For each pulp bleaching stage as shown in Table 1, Swanson *et al.*[3] carried out an investigation to determine the amounts of chlorinated dioxins in the pulp and obtained Figure 2. From this Figure, it can be seen that chlorinated dioxins are generated in each bleaching step. Axegård and Renberg investigated the relationship between the pulp lignin content and the bleaching agent at the time of pulp bleaching, and obtained the following results and conclusions.[4] The most important variable is

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the chlorine consumption volume, which is expressed as the ratio of the lignin content in the unbleached pulp to the chlorine amount. This ratio is generally referred to as the Cl_2-multiple. The amount of the chlorinated compounds (chlorinated phenols, chlorinated guaiacols, chlorinated catechols, chlorinated dioxins, chlorinated dibenzofurans; the total amount of these is expressed as AOX) produced by the chlorine bleaching increases dramatically when the chlorine multiple is greater than the critical value (0.2).

When the chlorine-multiple is below this critical value, the amount of AOX produced is very small. No significant difference is observed in the lignin removing process when oxygen is used or not used.

Swanson *et al.* have also reported similar results.[5] Kitunen et al. inferred from the results of the isomer analysis on chlorinated dioxins and chlorinated dibenzofurans in the products from the pulp industry, that the main chlorinated dicxins are produced by the condensation of chlorinated phenols (2,4,6-Trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,4-dichlorophenol, pentachlorophenol), and this occurs under alkaline conditions. On the other hand, it is inferred that chlorinated dibenzofurans are produced under conditions for the chlorination of phenols.[6]

By taking into consideration these analyses of the production mechanism, Swanson et al. investigated methods to suppress chlorinated dioxins on an actual-scale bleaching plant, and proposed alternative ideas such as lowering the chlorine level in the early bleaching steps, or changing to an oxygen bleaching method, etc.[7]

Examples of Residues in Paper Products p.45

Beck *et al.* observed that because during the analysis of trace

amounts of chlorinated dioxins there often were variations in the measurements due to the background, they gave consideration to contamination from the paper products in the laboratory, and so they analyzed for chlorinated dioxins in various paper products.[8] The results from this are shown in Table 2. From these results, it is stated that, because the chlorinated dioxin content in newsprint, of which 75% and greater are made from wood pulp, is just at the detectable limit, and because newsprint is not bleached, etc., the cause of the chlorinated dioxins formation in paper products *is* the pulp bleaching process.

Also, at the poster session of Dioxin '88, Rappe *et al.* reported as follows.[9] At Dioxin '87 (Las Vegas) the presence of 2,3,7,8-TCDD and 2,3,7,8-TCDF in pulp was reported, as well as reports that in the United States chlorinated dioxins in paper diapers were investigated, etc., and so the media in Sweden gave much attention to paper products. As a result, a few so-called dioxin free paper products are being sold in Sweden. Analyses for chlorinated dioxins in various commercially available paper products, including these dioxin free paper products, were carried out, and the results were reported. These results are shown in Table 3, and show that chlorinated dioxins were also detected in the chlorine free or dioxin free products.

Transfer of Chlorinated Dioxins from Paper Products to the Human Body

Beck *et al.* posed the question of how much of the chlorinated dioxins are transferred from these paper products to the human body.[10] They regard coffee filter paper as the paper product which is the most important factor with regard to daily intake (of chlorinated dioxins), and so they have attempted to evaluate the risk. According to them, about 50% of the

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2,3,7,8-TCDD/TCDF in a coffee filter paper is transferred to the coffee, and estimated that 5 pg of 2,3,7,8-TCDD and 3.2 pg of 2,3,7,8-TCDF is ingested per person per day.

Ryan *et al.* analyzed the milk in paper containers, and have reported the results as shown in Table 4.[11] They also reported that the analyses done at the same time on milk in plastic containers and in glass containers showed no detectible chlorinated dioxins. These quantities of the chlorinated dioxins transferred to the human body were evaluated at present to be considerable amounts.

It is doubtful that these transferred amounts become immediately harmful to humans; for example, the Nordic Council, which is composed of four northern European countries, have set the allowable level of chlorinated dioxins per week for the TEQ allowable amount (TWI, Note 2) to be 35 pg/kg of body weight, and so for a person with a body weight of 60 kg the allowable amount per week is 2000 pg (TEQ); compared to this allowable amount, the values (in Table 4?) can be considered to be much lower.

Preventative Measures

On June 20, 1988 the Environmental Energy Minister of Sweden declared that all the paper products in Sweden must be dioxin free within one year. As a background to this announcement, as described in the section on the production mechanism, in Sweden they are actively working towards reducing dioxins.

The paper industry in the United States is undertaking the following investigations in accordance with the US EPA.[12] p.46

- Set up and expansion of the database on effluents.
- Investigations on the techniques for removing toxins during the bleaching process and from the final effluents.

- Investigations on the relationship between the lignin removing treatment and the amount of bleaching agent with regard to the chlorinated dioxin production ability.
- The major environmental exposures and the risk evaluations in relation to these exposures.
- Review of the effects of chlorinated dioxins on human health.
- The major exposures to humans from the use of paper products and the risk evaluations based on these exposures.

In Japan also, attempts to use non-chlorine bleaching processes are being investigated.

Conclusions

In the modern industrialized society, during the production process or during the usage and disposal of chemical substances, it has become clear that unexpected harmful chemical substances are produced. Because these so-called non-intentional chemical substances are produced in so many different ways, there is the possibility that they may pollute the environment or cause damage to health in unexpected areas. The "Dioxin Strategy" of the US EPA, which was described at the beginning section, includes these kinds of items, and it can be said that one of the methods to prevent non-intentional chemical substances is given. With this new technique, the presence of harmful substances were detected in industrial products such as paper products. Furthermore, important aspects are that, based on these discoveries, management of the production processes and technology assessments were advanced further, and developments on their improvements and replacements were begun. Based on severe disastrous experiences such as the damage to human health and the destruction of ecological systems by chemical substances, attempts are being made to find

ways of properly producing, consuming and disposing of the chemical products, which have become indispensable to our life in the present worldwide society. This problem of chlorinated dioxins in paper and pulp production is noteworthy as one of the test cases. Also, before any cases occur, as a means of determining preventative measures, the methods for risk evaluation of the various chemical substances must be established in detail.

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Note 1) Chlorinated dioxins: This is used as a general term for polychlorinated dioxins and polychlorinated dibenzofurans.

Note 2) TEQ (TCDD equivalent)

In order to comprehensively express the toxicity of the many complexes of chlorinated dioxins, the TEQ value used is the sum of the relative toxicity of each isomer times its concentration, and is expressed as a concentration relative to 2,3,7,8-TCDD.

The chlorinated dioxins are comprised of a total of 210 different chemical substances, and among these there are 12 compounds which have high toxicities, and are the so-called 'dirty dozen'. The toxicity levels of these highly toxic 12 compounds differs according to the number of substituted chlorines, and their various relative toxicities have been proposed with the relative level of 2,3,7,8-TCDD set at 1, and recently the method by Eadon or the one by the US EPA have been most used, but furthermore, there is the Nordic Toxic Equivalent (NTEQ)* which was proposed by the Nordic Council in December 1987. The concentration of each isomer detected by analyses of the actual samples is multiplied by the appropriate factor in Table 5, and the expressed sum (TEQ) is employed because it accurately expresses the analytical results of the complex

compositions; recently the Japanese Environmental Department also uses TEQ for its reporting.

*) "Nordisk Dioxinrisk Bedomning" Nordic expert group (1988).

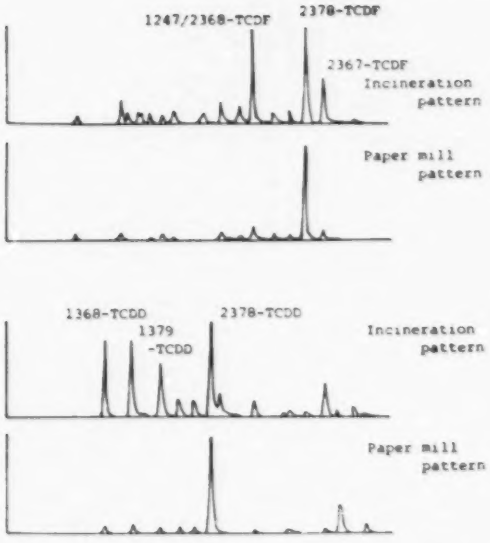

図1 カニ肝すい臓中のTCDDとTCDFの異性体組成

Figure 1. TCDD and TCDF Isomer composition in the Livers of Crabs

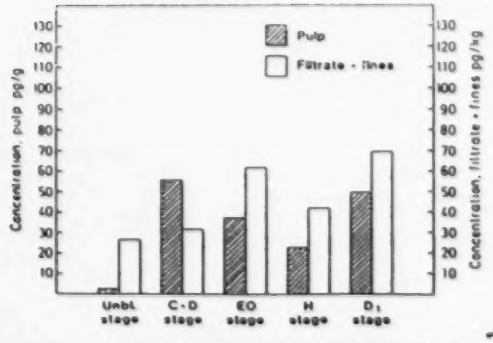

図2 パルプ漂白処理工程における塩素化ジオキシン類の生成（濃度はTEQ pg/g）

Figure 2. Production of Chlorinated Dioxins during the Pulp Bleaching Process (concentrations in TEQ pg/g)

Table 1. Various Bleaching Stages and Additives of Pulp

表1 パルプの種々な漂白段階と添加薬剤

漂白ステージ (bleaching stage)	使用薬剤と添加薬剤 (chemicals used and additives)
C+D	56kg Cl_2/ t 90% pulp, 3 kg ClO_2/ t 90% pulp
EO	32kg NaOH/ t 90% pulp, 4 kg O_2/ t 90% pulp
H	2 kg NaOCl/ t 90% pulp
D_1	15kg ClO_2/ t 90% pulp
E	5 kg NaOH/ t 90% pulp
D_2	4 kg ClO_2/ t 90% pulp

Table 2. TEQ Concentrations of Chlorinated Dioxins in Various Paper Products (West Germany)

表2 種々の紙製品中の塩素化ジオキシン類TEQ濃度 (西ドイツ)

製品名 (paper product item)	TEQ 濃度 (ppt) (TEQ concentration (ppt))
新聞紙 (newsprint)	0.3
実験用沪紙 (laboratory filter paper)	1.8
コーヒー沪紙 (coffee filter paper)	1.7
化粧用ティッシュ (facial tissue)	5.6
再生紙 (recycled paper)	12.2

注：TEQ は US EPA による

Note:TEQ is according to US EPA

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Table 3. Chlorinated Dioxin TEQ Concentrations in Various Paper Products (Sweden)

表3 市販紙製品中の塩素化ジオキシン類TEQ濃度 (スェーデン)

製品名 (paper product item)	TEQ 濃度 (ppt) (TEQ concentration (ppt))
紙おしめ (paper diapers)	1.0
布おしめ (cloth diapers)	0.2
ショッピングバッグ (shopping bag)	
未漂白 (unbleached)	1.9
漂白 (bleached)	5.7
タバコ用巻紙 (cigarette paper)	4.4
タンポン (tampon)	0.3
コーヒー沪紙 (coffee filter paper)	
未漂白 (unbleached)	3.8
漂白 (bleached)	8.2

注：TEQ は NTEQ による

Note:TEQ is according to NTEQ

Table 4. Chlorinated Dioxins in Milk from Paper Cartons (Canada)

表4 紙パック入り牛乳中の塩素化ジオキシン類
(カナダ)

異 性 体	濃度(pg/g whole milk)
2,3,7,8-TCDD	0.04
1,2,3,6,7,9/ 1,2,3,6,8,9-HxCDD	0.35
1,2,7,8-TCDF	0.5
2,3,7,8-TCDF	0.75

isomer

concentration (pg/g whole milk)

Table 5. Relative Toxicity Evaluation of Chlorinated Dioxins

表5 塩素化ジオキシン類の相対毒性評価

	EADON	US E.P.A	Nordic TEQ
2,3,7,8-TCDD	1	1	1
other TCDDs	-	0.01	-
2,3,7,8-P_5CDD	1	0.5	0.5
other P_5CDDs	-	0.005	-
2,3,7,8-H_6CDD	0.3	0.04	0.1
other H_6CDDs	-	0.0004	-
2,3,7,8-H_7CDD	-	0.001	0.01*
other H_7CDDs	-	0.00001	-
O_8CDD	-	0	0.001
2,3,7,8-TCDF	0.33	0.1	0.1
other TCDFs	-	0.001	-
2,3,7,8-P_5CDF	0.33	0.1	0.01**, 0.5***
other P_5CDFs	-	0.001	-
2,3,7,8-H_6CDF	0.01	0.1	0.1
other H_6CDFs	-	0.0001	-
2,3,7,8-H_7CDF	-	0.001	0.01
other H_7CDFs	-	0.00001	-
O_8CDF	-	0	0.001

Notes:

注： *1,2,3,4,7,8-H_6CDD
**1,2,3,7,8-P_5CDF
***2,3,4,7,8-P_5CDF

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